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Research paper

Heavy metals assessment of soils in and around Kama-Otto and Kwotto artisanal mining of mica, cassiterite and tantalite in Nasarawa state, Nigeria

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Abstract

This study assesses the level of heavy metal in Soils within the vicinity of artisanal mining of Mica, Cassiterite and Tantalite in Nasarawa State, Nigeria. Soil samples of Kama-otto and Kwotto artisanal mining were collected and analyzed using mass-plasma Atomic emission spectroscopy (MP-AES). Samples were also collected in Angwan-Mada, a non-artisanal mining environment, for comparison. Pollution assessment of soil samples using the following geochemical parameters such as contamination factor (CF), pollution load index (PLI), and Enrichment factor (EF), Nemerow index method (I_{IN}) and Geo-accumulating index (I_{geo}) were carried out. The results indicate an elevation in pollution status in the order of Kama-otto mining, Kwotto mining, Kama-otto, Kwotto and Angwan-mada. The concentrations of Cd, Cr and Mn were significant in the sampled areas ($P < 0.05$).

Keywords: *Artisanal Mining; Geo-Accumulating Index; Heavy Metals; Nemerow Index Method.*

1. Introduction

Anthropogenic activities like mining and industrial activities have been reported as the major source of heavy metal contaminations in soil, plants and water (Zhou et al., 2007; Luo et al., 2009; Yang et al., 2014). The economic pressures and insufficient environmental awareness have particularly exposed the local communities to heavy metal contamination due to mining activities. These depend on numerous factors including the dose, chemical species, route of exposure, and as well as the age, gender, genetics, and nutritional status of exposed individuals. Arsenic, cadmium, chromium, lead, and mercury rank among the priority metals that are of public health significance because of their high degree of toxicity (Tsuzuk et al., 1994; Josephat, and Saria 2016).

Before the establishment of the Ministry of Solid Mineral Development (MSMD) in Nigeria in 1995, emphases were not placed on exploration of solid minerals (Adamu et al.,2015). However, it became imperative due to the detrimental effect of mining activities since extraction of any mineral from earth surface without changing the natural environment in one way or the other is usually impossible (Mulligan, 1996 Ahmed and Oruonye 2016). Hence, the ecological damage due to little or no advance technology used in the operational area (Oladipo, 2006).

Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water (Tchounwou et al., 2012). They are characterized by relatively high density and high relative atomic weight with an atomic number greater than 20 (Shen et al., 2002, Chibuike and Obiora 2014). They are found in rocks and soils at low concentrations but are later elevated due to anthropogenic activity. The potential hazard caused by heavy metals in human and animal health has greatly increased the global concern for its presence in environmental media (Sobolev et al., 2008; Wei et al., 2010; Cui,et al.,2012, and Oyekunle et al., 2012).Therefore, the aim of this study is to assess the level of some selected heavy metals in soil samples of Kama-otto and Kwotto (artisanal mining vicinity) quantitatively and the results obtained would be compared to values obtained for Angwan-Mada, a non-artisanal mining area as well as world average shell value, in order to ascertain the extent of contamination resulting from artisanal mining.

2. Materials and methods

2.1. Study area

The sampling area selected is artisanal mining sites of Kama-otto and Kwotto communities of Nasarawa L.G.A of Nasarawa State, where tantalite, cassiterite and mica mining activities is carried out by the artisanal and small scale miners. These villages were selected because of its proximity to the area where the artisanal and small scale mining of these minerals above is currently going on. But Angwan-Mada which is 7 km from the mining site is chosen for comparison, since no record of any mining activities practice in the area so far.

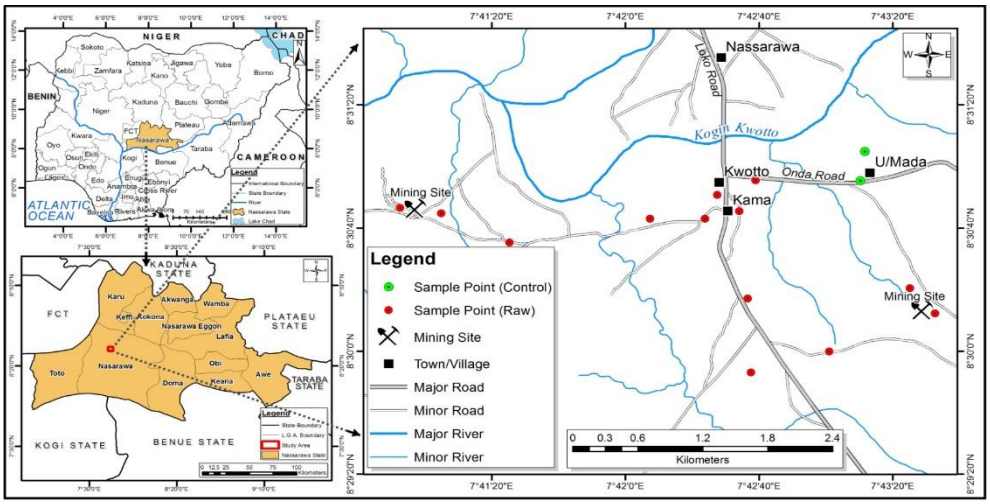

Fig. 1: Map of Nassarawa Showing Sampling Points.

Source: Fieldwork, 2017.

2.2. Collection of soil samples

Fifteen (15) soil samples were collected with the aid of an auger from the sampling sites. Each soil sample was collected from a depth [0], [15] layer of the soil profile at five different points and pooled together to give a composite sample. These was then transferred into a clean, labeled polythene bags and then transported to the laboratory where it was spread on a clean plastic sheet of flat surface on arrival for air-dried under room condition for one week.

2.3. Pre-treatment of soil samples

The digestion of soil samples were carried out following published methodology by (Adelakan and Abegunde 2011). 0.5 g of sieved and dried soil sample on a 2 mm sieve is digested with 10 cm^3 of nitric/ perchloric acid, ratio 2:1 in a beaker for 1 hour and 30 minutes at 105 ^{0}C. Next HCl and deionized water, ratio 1:1 was added and further digested for 30 minutes. The digest was removed from the digester and allowed to cool to room temperature. The content then was washed and filtered through a Whiteman filter paper No. 1 and then transfer into 100 cm^3 volumetric bottles and made up to mark with distilled water. Portions of this solution were used for heavy metals determination. These were carried out in triplicate.

2.4. Quantitative determination of heavy metals

Micro-plasma Atomic Emission Spectroscopy (Varian model-4200) 2011 Agilent technology equipment with a hollow cathode lamp (each for respective heavy metal), was used for quantitative determination of heavy metals in the soil samples.

2.5. Assessment heavy metal pollution

To make a comprehensive assessment of soil contamination, the Nemerow index was applied in these studies which reduce the interference of human factor. Because the traditional Nemerow index called geoaccumulation index, uses a single factor index method as the basis of the degree of contamination to access each metal, which couldn't accurately reflect the heavy metal contamination with the impact of human behaviors (Müller 1969) geoaccumulation index (I_{geo}) is computed by Equation;

$$I_{geo} = \text{Log}_2 \frac{C_1}{1.5\ B_1}$$

Where C_1 is the heavy metal concentration in the soil samples, B_1 is the geochemical background value in the average shale of the heavy metal element. The constant 1.5 compensates for the natural fluctuations of a given metal and for minor anthropogenic impacts. (Müller 1969) propose seven classes of I_{geo} as follows (Nuhu et al 2014, Edori and Kpee 2016).

Class 0 = $I_{geo} \leq 0$, uncontaminated
Class 1 = $0 < I_{geo} \leq 1$, uncontaminated to moderately contaminated
Class 2 = $1 < I_{geo} \leq 2$, moderately contaminated
Class 3 = $2 < I_{geo} \leq 3$, moderately to heavily contaminated
Class 4 = $3 < I_{geo} \leq 4$, heavily contaminated
Class 5 = $4 < I_{geo} \leq 5$, heavily to extremely contaminated
Class 6 = $I_{geo} > 5$, extremely contaminated

Table 1: Geochemical Background Value (Mg/Kg)

Metal	Zn	Cd	Pb	Man	As	Cr
Value	95	0.3	20	850	13	90

2.6. Improved nemerow index (I_{IN})

These traditional Nemerow index was improved by replacing the single factor index with I_{geo} were the following Equation was developed:

$$I_N = \sqrt{\frac{Igeomax^2 + Igeoave^2}{2}}$$

Where; I_N is the comprehensive contamination index of a sample, I_{geomax} is the maximum I_{geo} value of the sample; I_{geoave} is the arithmetic mean value of I_{geo}. To be consistent with I_{geo}, the classification of I_N was adjusted based on the results proposed by (Förstner et al., 1990) and this classification is as follows (Fernando et al., 2017).
Zero < $I_{IN} \leq 0.5$, uncontaminated (Class 0); $0.5 < I_{IN} \leq 1$, uncontaminated to moderately contaminated (Class 1); $1 < I_{IN} \leq 2$, moderately contaminated (Class 2); two < $I_{IN} \leq 3$, moderately to heavily contaminated (Class 3); $3 < I_{IN} \leq 4$, heavily contaminated (Class 4); four < $I_{IN} \leq 5$, heavily to extremely contaminated (Class 5); and $I_{IN} > 5$, extremely contaminated (Class 6).

2.7. Contamination factor (CF) and pollution load index (PLI)

The contamination factor (CF) for each heavy metal was calculated using the ratio of concentration of the metal in sample to the background concentration of the metal (Boamponsem et al., 2010)

$$CF = \frac{Concentration\ of\ metal\ in\ sample}{Concentration\ of\ metal\ in\ background}$$

These may be classified based on their intensities on a scale ranging from <1 to >six. This is given as Cf < 1, 1 < Cf < 3, 3 < Cf < 6, and Cf > 6 for low, moderate, considerable and very high contamination factor respectively (Ata et al., 2009).
Similarly, pollution load index (PLI) was calculated as reported by (Bhupander et al. 2011) According to (Ong et al 2012) PLI value > 1 indicates pollution whereas PLI value < 1 indicates no pollution.

$$PL_I = n\sqrt{CF_1 \times CF_2 \times CF_3 \ldots CF_n}$$

Where CF is the contamination factor of each metal that will be examined and n is the number of contamination factor.

2.8. Enrichment factor

An enrichment factor which is a parameter that is used to evaluate natural or anthropogenic sources of heavy metal content in the soil and water (Ata et al., 2009) is calculated. This index was used to distinguish between natural and anthropogenic sources. In order to calculate the enrichment factors for the entire element, Manganese (Mn) was used as a reference element which is conservative element (Hernadez et al., 2003; Ata et al., 2009). According to (Selvaraj et al., 2004) EF values from 1 to 10 indicate geogenic sources (natural source), while those greater than 10 indicate anthropogenic sources. (Sutherland 2000) suggested five contamination categories of enrichment factor and they are; < 2 Minimal enrichment; 2 - 5 Moderate enrichment; 5 - 20 Significant enrichment; 20 - 40 Very highly enriched; >40 Extremely highly enriched.

$$EF = \frac{(metal/Mn)\ sample}{(metal/Mn)\ Std.shale}$$

3. Result and discussion

3.1. Heavy metal contents in soil samples

The level of heavy metals in all the soil samples of the study area is shown in Figure 2. The concentrations of some heavy metal (Zn, Mn and Cr) for most soil sample analyzed in the study area were below the background world shale value while others (As, Cd and Pb) were above (Turekian, and Wedephol, 1961)
The results indicate that the concentration of Zn was significant in A.M as compare to Mkt, Kt, Mkm, Km respectively as well as Mkt with Kt, Mkm, Km and A.M (P < 0.05). However, there were no significant difference in the concentration of Zn in the samples from Kt, Mkm and Km. (Table 2)
The mean concentration of Cd, Cr and Pb were not significantly different from each other but each was significantly different from the mean in all sampling area (P<0.05). The level of As in Mkt, Mkm and Kt were not significant different, but it concentration in Mkt and Mkm showed a significant difference from the mean of all other sampling site. While Kt showed that there was significant difference with respect to other sampling areas. Thus, Km and A.M showed that there was no significant difference.
The Mn concentration in Km showed that, there was no significant different among the sample. Mkt, Kt, Mkm, and A.M in Zn showed that there were not significant to each other but there was significant different from the mean of all sampling area.

Table 2: Anova of Heavy Metal Contents in Soil Samples

	Zn	Cd	Pb	Mn	As	Cr
Mkt	288.11±208.68^{a}	0.89±0.86^{e}	29.93±2 4.91^{ab}	370.29±6 5.24^{d}	46.54±6 .89^{b}	25.05±1 0.44^{e}
Kt	72.20±4 6.92^{ab}	0.12±0.06^{d}	24.05±7 .53^{ab}	1738.22± 927.67^{c}	64.32±1 2.31^{ab}	35.43±2 7.27^{d}
Mkm	68.68±3 6.02^{ab}	0.98±0.49^{c}	21.68±1 1.48^{c}	713.73±2 58.09^{b}	4.40±25 .50^{c}	29.80±2 6.72^{c}
Km	56.67±2 0.85^{ab}	2.87±1.22^{a}	35.37±2 6.39^{ab}	913.30±5 54.33^{ab}	99.57±4 5.11^{a}	115.93± 50.21^{a}
A.M	15.7±6.2 9^{b}	0.90±0.07^{b}	12.25±4 .67^{ab}	143.60±8. 84^{a}	65.75±4 .60^{ab}	14.13±0 .88^{b}

Mkt = Mining Area of Kwotto, Kt = Kwotto, Mkm = Mining Area of Kama-Otto, Km = Kama-Otto and A.M = Angwan-Mada
(a,b,c,d = significant difference and ab = no significant difference)

3.2. Assessment of heavy metal pollution in soil samples

Table 2 shows the CF for the six metals in different soil samples is indeed very moderate but with an exception of As, Cd and Pb which are highly contaminated. Generally the degree of metal pollution increases from As > Cd > Pb > Zn > Mn > Cr. Whereas PLI of soil in all the studied area ranged from 0.586 to 2.183. The lowest PLI value was recorded at Angwan - Mada that has low anthropogenic activities as compare to other studied areas. These were due to gradual increase in anthropogenic activities, which include artisanal mining of minerals, improper disposal of batteries and cigarette, improper dumping of metallic material and refuse dump.

Table 3: Contamination Factor and Pollution Load Index of Soil

	Zn	Cd	Pb	Man	As	Cr	PLI
Mkt	3.033	2.967	1.497	0.436	3.580	0.278	1.343
Kt	0.760	0.400	1.203	2.045	4.948	0.394	1.065
Mkm	0.723	3.267	1.084	0.840	3.415	0.331	1.160
Km	0.597	9.567	1.769	1.075	7.659	1.288	2.183
A.M	0.164	3.000	0.613	0.169	5.068	0.157	0.586

Mkt = Mining Area of Kwotto, Kt = Kwotto, Mkm = Mining Area of Kama-Otto, Km = Kama-Otto and A.M = Angwan-Mada.

The I_{geo} of soils in Kwotto and it mining area were classified as Class 0 (58.3 %), Class 1 (16.7 %) and Class 2 (25 %) respectively. That is, uncontaminated to moderately contaminated. Similarly In Kama-otto and it mining area, it were classified as Class 0 (58.3 %), Class 1 (8.3 %), Class 2 (16.7 %) and Class 3 (8.8 %) that is, uncontaminated to moderately contaminated. However, the Angwan-Mada which is the control site was only classified as Class 0 (66.7 %) and Class 2 (33.3 %) that is, uncontaminated to moderately contaminated.
Furthermore, considering I_N, All soil sample of the studied area were generally classified by Class 1 ($0.5 < I_N < 1$) and Class 2 ($1 < I_N \leq 2$) that is, uncontaminated to moderately contaminated as indicated in Table 4. However, the small degree of contamination indicated by this index may be due to anthropogenic processes (atmospheric deposition of metals), which led to an increase in geological concentrations in the soils of these sample area. Also wet and dry deposition caused by metallic mining and the processing of minerals from bordering areas led to accumulation of heavy metals.

Table 4: Geoaccumulation Index and Improved Nemerow Index

	Zn	Cd	Pb	Mn	As	Cr	Go_e	G_{mx}	I_N
Mkt	1.016	0.984	-0.003	-1.784	1.255	-2.230	-0.127	1.255	0.892
Kt	-0.981	-1.907	-0.319	0.447	1.722	-1.930	-0.495	1.722	1.267
Km	-1.053	1.123	-0.469	-0.837	1.187	-2.180	-0.372	1.187	0.879
MKm	-1.330	2.673	0.238	-0.481	2.352	-0.218	0.539	2.673	1.928
A.M	-3.191	1.000	-1.292	-3.150	1.754	-3.256	-1.356	1.754	1.568

Mkt = Mining Area of Kwotto, Kt = Kwotto, Mkm = Mining Area of Kama-Otto, Km = Kama-Otto and A.M = Angwan-Mada.

The computed enrichment factor (EF) depicts that the trends of metal enrichment in soil of the area varies from one location to another (Table 5). The enrichment factor in both As and Cd was rnged from moderately to significantly enriched while Zn, Pb, and Cr were from deficiency to minimal enriched in the studied area.

Table 5: Enrichment Factor of Soil

	Zn	Cd	Pb	As	Cr
Mkt	6.962	6.810	3.435	8.218	0.639
Kt	0.372	0.196	0.588	2.419	0.193
Mkm	0.861	3.890	1.291	4.067	0.394
Km	0.555	8.904	1.646	7.128	1.199
A.M	0.972	17.76	3.626	29.938	0.929

Mkt = Mining Area of Kwotto, Kt = Kwotto, Mkm = Mining Area of Kama-Otto, Km = Kama-Otto and A.M = Angwan-Mada.

4. Conclusion

The assessment of heavy metal level in Soils within the vicinity of artisanal mining of Mica, Cassiterite and Tantalite in Nasarawa State, Nigeria was successfully carried out, and the result shows that soil samples were more contaminated in comparison to samples from Angwan-Mada, which is the control as well as background world shale value. These might not be unconnected with the anthropogenic activities that is artisanal and small-scale mining. This work goes a long way in making available data that can be used in remediation policy for environmental contamination caused by As and some other heavy metals.

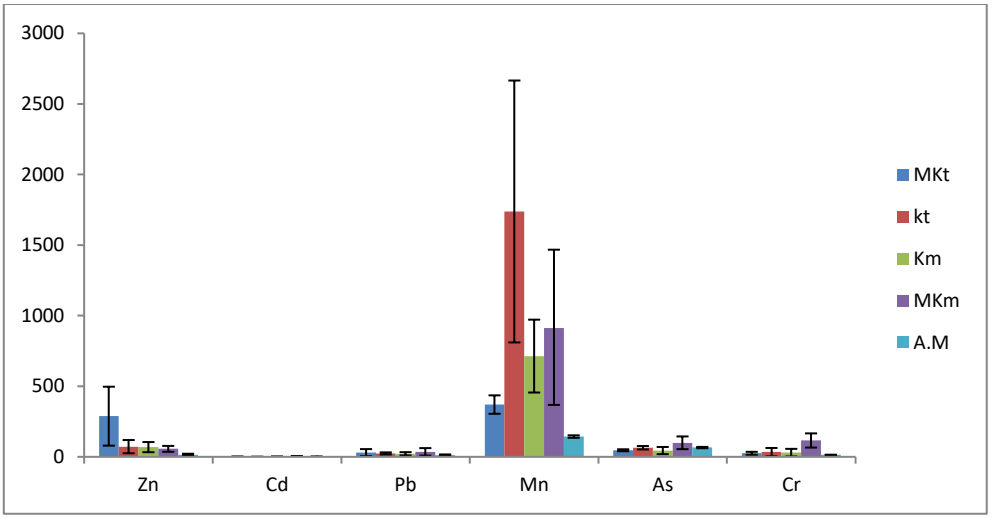

Fig. 2: Mean Concentration of Heavy Metals in Soil Samples of (Kwotto, Kama-Otto, Kwotto Mining Area, Kama-Otto Mining Area and Angwan-Mada), Nasarawa State, Nigeria. Each bar Represents Mean ± Standard Deviation Different Samples Area.

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